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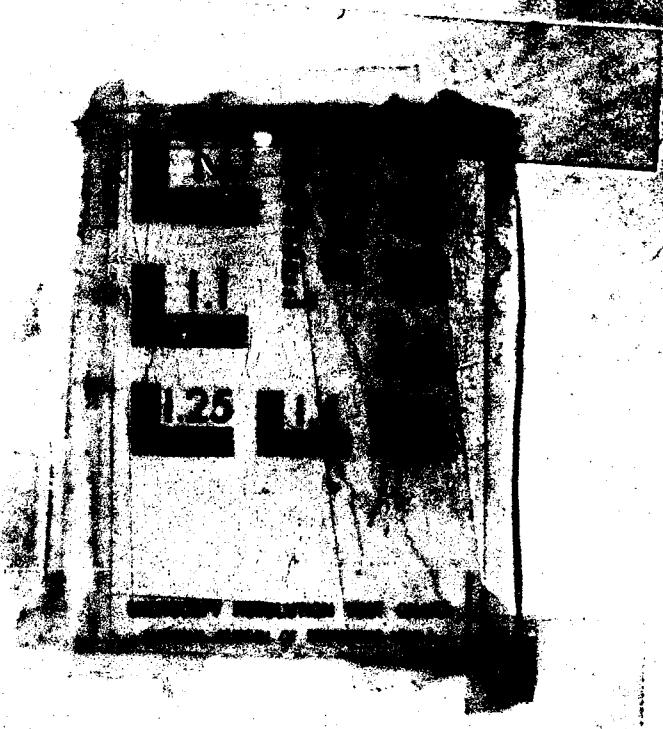
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The Interaction of Complexes $Mn(PPh_3)_2Br_2$ and $Mn(PEt_3)_2Br_2$ with Sulfur
Dioxide

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Abstract

The interactions of the complexes $Mn(PPh_3)_2Br_2$ and $Mn(PEt_3)_2Br_2$ as films with SO_2 and S_18O_2 have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with SO_2 have been formed. When the $MnLBr_2$ films were exposed to low pressures of SO_2 for relatively short times, an $MnLBr_2/SO_2$ complex formed reversibly in that the SO_2 could be removed by prolonged evacuation. On the other hand, lengthy exposure of the $MnLBr_2$ films to higher pressures of SO_2 caused the irreversible formation of a complex having stoichiometry $MnLBr_2 \cdot 1/2SO_2$. It is probable that the SO_2 bonds in some type of bridging fashion in both of the types of $MnLBr_2/SO_2$ complexes.

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There has been considerable recent interest in complexes of the form $MnLX_2$ (L =tertiary phosphine, X =anion) and their interaction with dioxygen.^{1,2} Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxygen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.^{3,4} All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.^{3,4} The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of $MnBr_2$ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell^{3,4} at 10^{-6} Torr to remove all water. Then the dry $MnBr_2$ films were exposed to either $PPh_3\text{O}_2$ or $Ph_3\text{S}$ in film to form the $MnLX_2$ complex films. Extensive evacuation at 10^{-6} Torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO_2 /evacuation cycles with infrared spectra (Perkin-Elmer Models 582 or 983 with data station) being monitored at appropriate intervals. Since $\text{SO}_2(\text{g})$ exhibits infrared bands near 520, 1150, and 1360 cm^{-1} which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO_2 exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the $Mn(PPh_3\text{O}_2)\text{Br}_2$ complex film interacting with SO_2 . A comparison of Fig. 1b and 1a reveals that new infrared bands at $\text{SO}_2(\text{S}^{\text{I}}\text{O}_2)$: 412(410), 445(440), 525(515), 785(780), 995(950), 1002(968), and 1075(1028) cm^{-1} appear which can be attributed to a new complex(es) formed from the reaction of SO_2 with

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at 1033 cm⁻¹ in the spectrum at 1000 Torr which does not shift appreciably when SO_2 is added. This band can be assigned to a mixed vibrational mode (ν_{asym}) which is calculated due to the presence of SO_2 ; this band was also observed to be present in the presence of diatomic A . All of the bands observed above shifted markedly upon evacuation at 10⁻⁶ Torr for 10 hr (Fig. 1c). We have been able to observe cycling of the intensities of these bands upon evacuation/evacuation for up to three cycles; i.e., 12 hr evacuation is sufficient to essentially remove the SO_2 . However, upon lengthy exposure (72 hr) at high pressure (120 Torr) spectrum 1d resulted which could not be removed by further evacuation. The bands at 995, 1002, and 1033 cm⁻¹ for this spectrum were shifted to 990, 1000, and 1030 cm⁻¹ and obviously correspond to the previously discussed modes; the fact that three such bands were present indicates that more than one type of complex is probably being formed. The remaining two bands at 612 and 865 cm⁻¹ shifted little if any (approximately 10%). These bands could correspond to $\text{M}-\text{O}_2$ modes. The bands at 910 and 970 cm⁻¹, in 1d, did shift appreciably when S^{18}O_2 was added to the system.

Figure 2 shows a similar series of experiments for $\text{MgBr}_2/\text{SO}_2/\text{N}_2$ interacting with SO_2 . Band positions for S^{34}O_2 complex spectra are shown in parentheses. Again reversibility was observed as long as exposure time and pressure were minimized. It is clear that at least two types of $\text{MgBr}_2/\text{SO}_2$ complexes were formed in these experiments - one in which the SO_2 bands reversible and one in which the SO_2 is coordinated in an irreversible fashion. Comparison of the intensities of the 865, 910, and 970 cm⁻¹ bands in spectra 1d and 2d reveals that the reversible complex can decompose to the irreversible one even during evacuation following high SO_2 exposures.

The two forms of the new Cu(II) complexes and their analogs were prepared under identical conditions to insure consistency in the sample preparation conditions for the formation of film. The IR analysis of the two final structures was compared to find that the stoichiometry for each was identical.⁵ This was along with the observation of similar infrared bands in the 800-1075 cm⁻¹ region of the spectra imply that the two forms of each complex contain SO₃²⁻ bonded in a bridging mode,⁶ with more than one atom of Cu involved in the bridge. Final structure determination must await X-ray crystallographic data.

It should be noted that Marshall and coworkers have reported recently the reaction of Cu(II) with several sulfur containing telecenes in solution and in telecene slurries.⁷ They report a stoichiometry of Cu(II)/2SO₃²⁻ for their solution studies, and they were not able to observe reversibility. Furthermore, they report prominent infrared bands in the 1110-1150 cm⁻¹ region which are not observed for the Cu(II)/SO₃²⁻ complex film. However, their experimental conditions (liquid phase, 760 MHz SO₃²⁻ exposure for 48 hr) were markedly different than those used in this work; thus it is possible that a reversible complex was formed also in their work, but converted to an irreversible product before analysis.

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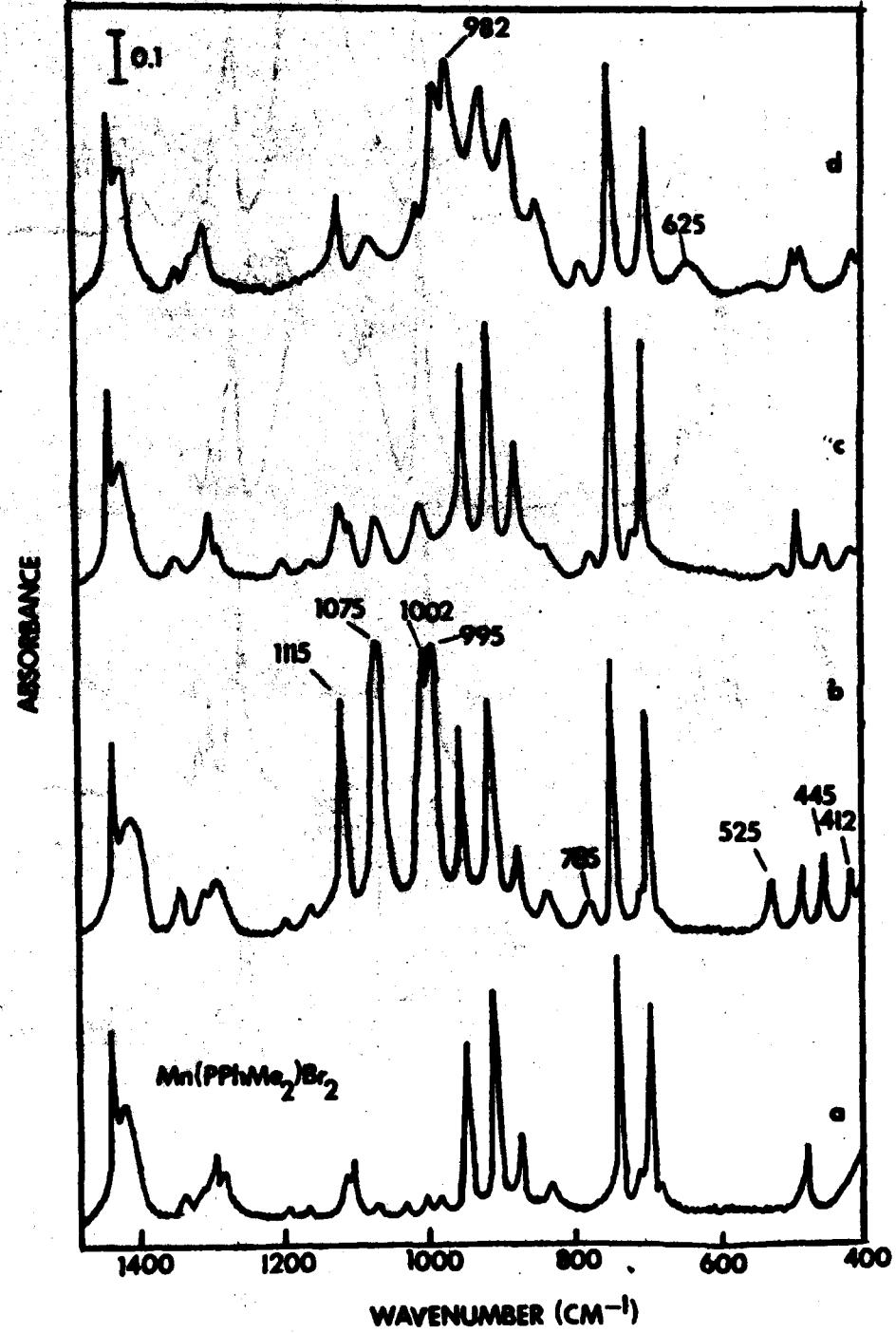
- (1) McAliffe, C.A. *J. Organomet. Chem.* 1982, 228, 253 and numerous references quoted therein.
- (2) Bryan, D.M.; Bull, R.R.; Green, M.L.H.; Grabenik, P.D.; Martin-Polo, J.J.; Minges, D.M.P. *J. Organomet. Chem.* 1980, 201, 437.
- (3) Burkett, E.B.; Newberry, V.F.; Hill, W.E.; Worley, S.D. *J. Amer. Chem. Soc.* 1963, 85, 4097.
- (4) Newberry, V.F.; Burkett, E.B.; Worley, S.D.; Hill, W.E. *Inorg. Chem.* 1964, 23, 3911.
- (5) Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PPh_3)_2Br_2 \cdot 1/2S_0_2$: C 25.0, H 2.9, Br 41.5, S 4.2. Found: C 24.8, H 3.0, Br 41.4, S 4.1; Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PEt_3)_2Br_2 \cdot 1/2S_0_2$: C 19.7, H 4.1, Br 43.8, S 4.4. Found C 19.7, H 4.2, Br 43.7, S 4.4.
- (6) See for examples: Witthuhn, G.; Lindner, K. *Anz. Chem. Int. Edit.* 1971, 10, 315; Kubas, G.J. *Inorg. Chem.* 1979, 18, 182; Ryan, R.R.; Kubas, G.J.; Moody, D.C.; Eller, P.G. *Struct. Bonding (Berlin)* 1981, 46, 47; Jarvinen, G.D.; Kubas, G.J.; Ryan, R.R. *J. Chem. Soc. Chem. Commun.* 1981, 365; Bristot, C.E.; Hughes, G.R.; Minshall, P.C.; Minges, D.M.P. *J. Organomet. Chem.* 1982, 224, C31; Bristot, C.E.; Theobald, D.R.C.; Minges, D.M.P. *J. Chem. Soc. Chem. Commun.* 1981, 963.
- (7) McAliffe, C.A.; Barrett, S.S.; Benson, C.C.; Tanner, S.P. *J. Chem. Soc. Dalton Trans.*, in press.

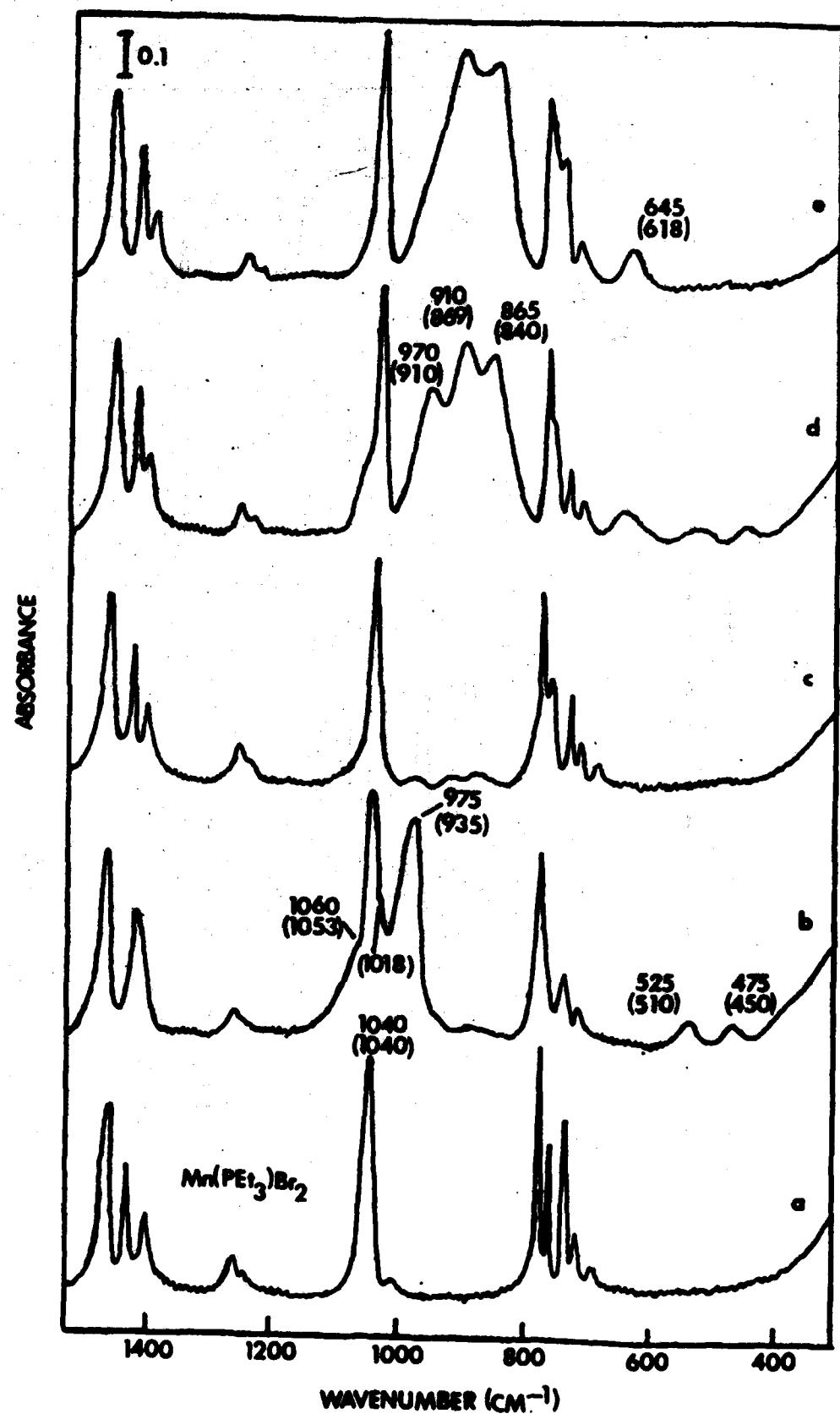
Figure Captions

Figure 1. The infrared spectra of a $Mn(PPh_3)_2Br_2$ film:

- (a) following initial preparation; (b) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation;
- (c) following an evacuation cycle for 12 hr at 10^{-6} Torr at 298 K; (d) following exposure to 120 Torr SO_2 for 72 hr at 298 K and lengthy evacuation.

Figure 2. The infrared spectra of a $Mn(PEt_3)_2Br_2$ film: (a) following initial preparation; (b) following exposure to 15 Torr SO_2 for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 hr at 10^{-6} Torr at 298 K; (d) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation; (e) following evacuation for 24 hr at 10^{-6} Torr at 298 K. Band positions for analogous $S^{18}O_2$ complex spectra are given in parentheses.





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